

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-296068

(43)Date of publication of application : 18.11.1997

(51)Int.Cl.

C08J 9/28

(21)Application number : 08-109962

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(22)Date of filing : 30.04.1996

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(54) PRODUCTION OF GEL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a gel having many micropores by applying an aqueous dispersion of fine particles on a support to form a layer of the dispersion, agglomerating the fine particles by destabilizing the dispersion before the water is completely evaporated, and drying the layer.

SOLUTION: Water and a specified amount of a nonionic emulsifier are fed into a reactor and heated. To the mixture is added, about 25wt.% monomer mixture containing methyl methacrylate, butyl acrylate, styrene or the like is under agitation. Next, a polymerization initiator (e.g. ammonium persulfate) is added to the mixture, and the residual monomer mixture is added thereto. The resulting mixture is agitated for a specified time to prepare an aqueous resin dispersion containing dispersed polymer particles. A thermosensible gelling agent (e.g. ammonium sulfate zinc complex) is added to the dispersion under agitation to prepare an aqueous dispersion for coating. This dispersion is applied to a PET film coated with a primer layer and dried at about 10-98° C to cause gelation of the polymer particles in the dispersion, and the film is dried to obtain a porous filmy gel having many pores having a mean diameter of 500nm or below.

LEGAL STATUS

[Date of request for examination]

26.02.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the gelation object characterized by making said particle condense and subsequently making it dry by destabilizing a water dispersing element before a particle applies the water dispersing element currently distributed to stability on a base material, and forms a moisture powder body whorl into an aquosity medium and all the water in this moisture powder body whorl disperses.

[Claim 2] The manufacture approach according to claim 1 which is what a water dispersing element destabilizes with heating.

[Claim 3] The manufacture approach according to claim 2 which is what performs condensation of the particle in a water dispersing element under the ambient atmosphere more than the setting temperature of a water dispersing element, and more than the same water vapor pressure as the saturated water vapor pressure in setting temperature.

[Claim 4] The manufacture approach according to claim 1 to 3 that a gelation object is the porous membrane which has much puncturing with an average diameter of 500nm or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] It is a thing about the approach of manufacturing the gelation object which has much puncturing detailed [this invention] and uniform. In a detail In the water dispersing element which inorganic or an organic particle is distributing to stability in an aqueous medium It is related with the manufacture approach of a new gelation object of making the gap of a particle and a particle remaining as puncturing, by making it condense and gel, maintaining a particle condition mostly, without carrying out welding of these particles. The manufacture approach of this invention is useful as an approach of forming various porous membrane which can be developed for an application and porosity material.

[0002]

[Description of the Prior Art] The device (film formation device) in which the polymer particle in water dispersing elements, such as an emulsion and a latex, creates the uniform continuous coat is considered as follows.

** After forming the layer of a water dispersing element, while water exists enough in this layer, it is moving about the emulsion particle freely by Brownian motion.

** If desiccation progresses and the amount of water decreases considerably, a particle can be mutually drawn near with the surface tension of water, and the welding of a particle will begin from the place which changed into the closest packing condition.

** After the protective layer which had contributed to distributed stabilization is destroyed, by the capillary pressure of the water with which particles still remain also in a closest packing condition, that a polymer chain (segment) exercises and carries out counter diffusion, or the viscous flow of a polymer chain, weld the welding of a particle, while a particle deforms and it forms a continuation coat.

[0003] Also in the present, after the welding of the particle in the above-mentioned **, a particle deform, and although not all the requirements when coat-ize be clear theoretically, this contractor treating water dispersing elements, such as an emulsion, of a coating or the adhesives field grasp Tg or minimum film forming temperature, add a film formation assistant etc. if needed, and form the uniform continuation coat.

[0004] On the other hand, in the case of an application which obtains the paint film of a thick film comparatively using an emulsion or a latex, the sensible-heat gelation system is used. For example, the activity of the sensible-heat gelling agent for drying a latex efficiently is indicated by JP,4-261453,A. That is, the water which is the medium of a latex has the large specific heat to the top where the boiling point is high, and since it is easy to produce a difference in the rate of drying on the front face of a paint film, and the rate of drying inside a paint film when it is especially a thick film, the so-called "leather-covered phenomenon" is caused. However, if a sensible-heat gelling agent is added in a latex, since the latex in coating liquid will condense at the time of stoving and the desiccation inside a paint film will be sped up, it is the technical thought that the heat energy for desiccation is saved and the paint film which was further excellent in the water resisting property with bridge formation of a carboxylic acid and a polyvalent metal complex can be created.

[0005] The particle in ** draws near the sensible-heat gelling agent in this technique among the above mentioned film formation devices, and it is promoted using the gelation and agglutination by the gelling agent in the condition that water has not dried yet the welding after **** and the closest packing, or deformation and welding of the particle in ** enough. Therefore, already the condensed particle deforms considerably, and is welded and it is thought that a continuation coat is formed after that.

[0006] By the way, film, a filter, etc. which have detailed puncturing in recent years are used as high-performance material in various applications. The sintering process is also used as an approach of the approach of using the phase separation in a polymer solution, the approach of etching into a polymer film by the high energy line, and the method of using the drawing of a polymer film being one of those by which current adoption is carried out as the production approach of the porous membrane of a polymer ingredient, and producing the porous membrane of inorganic powder, such as ceramics.

[0007]

[Problem(s) to be Solved by the Invention] In this invention, it hangs up as a technical problem offering the gelation object obtained by the header and this manufacture approach in the optimal manufacture conditions at the time of using the water dispersing element of inorganic or an organic particle as a manufacture raw material of a gelation object, making these particles in a water dispersing element gel and condense, and manufacturing a gelation object as various porous membrane which can be developed for an application and porosity material.

[0008]

[Means for Solving the Problem] Before a particle applies the water dispersing element currently distributed to stability on a base material, and forms a moisture powder body whorl into an aquosity medium and all the water in this moisture powder body whorl disperses, by destabilizing a water dispersing element, the manufacture approach of the gelation object of this invention makes said particle in a water dispersing element condense, and has a summary at the place subsequently dried. As for a water dispersing element, it is desirable that it is what is destabilized with heating. It is the desirable embodiment of this invention method each that it is what performs condensation of the particle in a water dispersing element under the ambient atmosphere more than setting temperature and more than the same water vapor pressure as the saturated water vapor pressure in setting temperature. Various application expansions are possible for the gelation object obtained by the approach of this invention as the porous membrane and the porosity material which have micropore as it is the porous layer which has much puncturing with an average diameter of 500nm or less. Of course, the porous membrane and the porosity material which have much bigger puncturing can also be manufactured, and according to the manufacture approach of this invention, according to an application, a mode can be changed suitably.

[0009]

[Embodiment of the Invention] After a particle apply the water dispersing element currently distribute to stability on a base material and form a moisture powder body whorl into an aquosity medium, before [in this layer] water disperse altogether, the manufacture approach of the gelation object of this invention destabilize the distributed condition of these particles, and have the greatest point at the place make to condense maintain the particle condition mostly. The difference when coat-izing the emulsion of a general polymer particle is explained like the formation fault of the gelation object of this invention using drawing. It is drawing in which A of drawing 1 showed the coat-ized device of the usual emulsion, and B and C showed the molding machine style of the gelation object of this invention in model.

[0010] The usual emulsion is (1). After forming an emulsion layer by carrying out coating of the emulsion, since water exists enough in this layer, in early stages of the desiccation phase, it is moving about the polymer particle freely by Brownian motion.

(2) If desiccation progresses and the amount of water decreases considerably, with the surface tension of water, a polymer particle can be mutually drawn near and will be in a closest packing condition.

(3) By the capillary pressure of extant water, that a polymer chain (segment) exercises and

carries out counter diffusion, or the viscous flow of a polymer chain, while this particle deforms, weld the polymer particle which changed into the closest packing condition.

(4) The interface of a polymer particle disappears and a uniform continuation coat is formed. It coat-izes by the device to say.

[0011] On the other hand, it sets to the pattern of B and the gelation object of this invention is (1). It is the same as A except the point that it is not limited only to a polymer particle but inorganic or an organic particle exists in a water dispersing element.

(2) In the phase where water still exists enough in a moisture powder body whorl, while the particle had held the particle shape by destabilizing a water dispersing element, gel and condense, and where a gap is left, combine each particle.

(3) With the condition that the particle left the gap and joined together, when water disperses, a gelation object is formed. When it says and that which can be welded as a particle is used [or], as it is shown as C, it is (1) and (2). It is the same as B. (3) (2) Although it sets, and a particle leaves a gap and joins together, it may weld to the particle by which a part of particle adjoins at the time of stoving for dispersing water. However, since it is slight deformation and welding which is extent in which the opening between particles remains, a gelation object is formed too. It says.

[0012] In addition, since a part of particle carries out deformation weld of the case of this C pattern, the physical reinforcement as a gelation object becomes the outstanding thing from the pattern of B in many cases. In the gelation object generated with the pattern of B, a particles bridge formation system may be used in order to ensure association of a particle and a particle and to form a strong gelation object.

[0013] Thus, in the process of this invention, since inorganic [in a water dispersing element] or an organic particle condenses, maintaining that particle condition mostly (the pattern of Above B and the pattern of C are set and it expresses hereafter, saying, "the particle condition was maintained mostly"), particles join together in the condition with a gap, and when water disperses after that, it coat-izes. For this reason, the gelation object with which the opening between particles remained as puncturing as it is can be obtained.

[0014] By this invention method, condensation of the particle in a water dispersing element is performed by destabilizing a water dispersing element. That is, water dries, and condensation of a particle must be performed before all water disperses from this moisture powder body whorl, but [not after being coat-ized] after applying a water dispersing element to a base material and forming a moisture powder body whorl. So, by this invention method, a water dispersing element is destabilized and using the sensible-heat gelling method is recommended as an approach of making the particle which was being distributed to stability till then condensing. Moreover, the optical gelling method mentioned later can also be used as the gelation approach.

[0015] The approach and ** sensible-heat gelling agent which the sensible-heat gelling method manufactures [gelling agent] a water dispersing element using the Nonion system emulsifier with the approach, for example, a cloudy point, of giving the property destabilized by the temperature change to the ** water dispersing element itself, warms [gelling agent] it more than a cloudy point, and make a water dispersing element gel are added, and the method of making a water dispersing element gel etc. is mentioned by warming more than the setting temperature of this sensible-heat gelling agent. In addition, the approach of forming into a water dispersing element is also included in "manufacture" of a water dispersing element here by making stability distribute the polymer which carried out the polymerization, or inorganic powder in the shape of a particle in an aquosity medium using a dispersant or an emulsifier with the approach of manufacturing an organic particle (for example, polymer particle) according to an emulsion polymerization, and other polymerization methods.

[0016] In the sensible-heat gelation approach, in order to adopt the approach of the above-mentioned **, it is good to use the approach of distributing compulsorily the polymer and inorganic compound which carried out the emulsion polymerization using the Nonion system emulsifier which has a cloudy point or which were manufactured independently using the Nonion system emulsifier (dispersant), and manufacturing a water dispersing element.

[0017] As an example of the Nonion system emulsifier, polyvinyl alcohol, denaturation polyvinyl

alcohol, a fatty acid and polyethylene glycol ester, higher-alcohol polyethylene glycol ether, alkylphenol polyethylene glycol ether, an alkylamine polyethylene-glycol condensate, an alkylamide polyethylene-glycol condensate, a sorbitan fatty-acid-monoester polyethylene-glycol condensate, etc. are mentioned. These emulsifiers have a cloudy point 100 degrees C or more from 30-degree-C order according to a class. Control of scattering of water is easy, when a cloudy point makes an emulsifier 98 degrees C or less gel, since it is easy to obtain the gelation object with which uniform puncturing was formed, it can be used preferably, but since it is possible to lower a cloudy point by adding the water-soluble matter even if it is the emulsifier which has a cloudy point 100 degrees C or more, such an emulsifier can also be used by this invention method.

[0018] The sensible-heat gelling agent which can be used by the approach ** Silicofluorides, such as a sodium silicofluoride and potassium silicofluoride, Metal complexes, such as an ammonium-sulfate zinc complex and an ammonium-carbonate zinc complex, A zinc oxide, inorganic or organic ammonium salt (these complexes), nitroparaffin, Organic ester, polyvinyl methyl ether, a polypropylene glycol, A polyether poly formal, a polyether denaturation polysiloxane, the alkylene oxide addition product of an alkylphenol formalin condensate, A functionality polysiloxane, water-soluble denaturation silicon oil, a silicone glycol copolymer, The Nonion system emulsifier which has a water-soluble polyamide, starch, methyl cellulose, hydroxyethyl cellulose, a carboxymethyl cellulose, protein, polyphosphoric acid, or the above-mentioned cloudy point is mentioned, and these one sort or two sorts or more can be mixed and used. Since it becomes that it is [control of setting temperature] easier to mix two or more sorts and to use a sensible-heat gelling agent, it is desirable, and nitroparaffin and organic ester have the effective concomitant use with a zinc oxide.

[0019] The desirable setting temperature of a sensible-heat gelling agent is 10-98 degrees C. Since the preservation stability after mixing a sensible-heat gelling agent with a water dispersing element, and pot life are not securable in setting temperature lower than 10 degrees C, it is not desirable. Moreover, in the case of the setting temperature exceeding 98 degrees C, since it is hard to obtain the gelation object with which uniform puncturing was formed by the scattering rate of water becoming large rather than the gelation reaction, it is not desirable. In addition, a "sensible-heat gelation" operation of the semantics of the wide sense that progress of a gelation reaction is promoted remarkably shall be said by warming "sensible-heat gelation" not more than the semantics that gelation does not progress at all in ordinary temperature but more than setting temperature.

[0020] By this invention method, the optical gelling method may be adopted as an approach of destabilizing a water dispersing element, in addition to the sensible-heat gelling method. The optical gelling method is the approach of irradiating light, making an emulsifier disassemble into, when making a water dispersing element manufacture and (for both an "emulsion polymerization" and "compulsive distribution" to be included in "manufacture" as described above) gel using a photodegradable emulsifier, and carrying out deactivation of the particle stabilization function.

[0021] Although the presentation of a water dispersing element itself is not especially limited when using the sensible-heat gelling method, the optical gelling method, and any, in the case of an organic system If a polymer particle is preferably used as a particle and an example is shown Rubber system latexes which made an acrylic acid and its ester the subject, and copolymerized one various organic functions and the polyfunctional monomer in which a polymerization is possible, such as acrylic emulsion; SBR, and NBR, IR, NR; (Meta) The thing of polyester or polyurethane which carried out the water dispersing element is mentioned. Moreover, the blend of two or more sorts of emulsions may also be possible, and you may be the emulsion which has the particle of a core shell mold. What distributed the inorganic compound, the inorganic pigment, etc., using the dispersant and emulsifier of the Nonion system, or other dispersants and emulsifiers as a water dispersing element of an inorganic system particle is available.

[0022] Since various application expansions are possible for the gelation object of this invention, it is desirable to choose the presentation of a water dispersing element according to an application. For example, although the gelation object used on ordinary temperature level is manufactured, when it saves in ordinary temperature, since the particle in a gelation object is a

problem with a lifting and the configuration that porosity will be lost, viscous flow Using the polymer emulsion of a presentation of Tg of 0 degrees C or more, even if Tg is lower Carrying out the molecular design of the particle which constitutes a gelation object according to an application is recommended so that it may say that the emulsion of the polymer of a configuration of having controlled the mobility (deformability) after coat-izing according to bridge formation, or the water dispersing element of an inorganic particle is chosen.

[0023] In order to obtain a uniform gelation object by this invention method, when dispersing water from a water dispersing element emulsion layer, it is more than the setting temperature of this water dispersing element, and it is desirable to carry out under the ambient atmosphere more than the same water vapor pressure as the saturated water vapor pressure in the setting temperature of a parenthesis. On this ambient atmosphere condition, since it is more than setting temperature, it is because scattering of the water from the applied moisture powder body whorl is controlled by gelation and condensation of the particle in a water dispersing element advancing according to a sensible-heat gelation operation, and on the other hand adjusting an ambient atmosphere more than the same water vapor pressure as the saturated water vapor pressure in setting temperature. It is desirable to perform gelation and condensation, suppressing scattering of water under the above-mentioned ambient atmosphere, since the scattering of water may become quick from the degree of completion of gelation and a uniform gelation object may not be obtained, when there are few amounts of the water to disperse, or especially when the nonvolatile matter of a water dispersing element is high, and the setting temperature of the sensible-heat gelling agent to be used is high or the coating thickness to a base material top is small. What is necessary is just to change into the conditions on which water disperses positively instead of the bottom of the above-mentioned ambient atmosphere, after gelation and condensation are completed.

[0024] In addition, if a gelation rate uses a sensible-heat gelling agent with low setting temperature quickly, even if scattering of the water from a moisture powder body whorl takes place [be / it / under / gelation reaction progress / concurrency], a uniform gelation object will be obtained. What is necessary is on the other hand, just to disperse the water of a moisture powder body whorl by the optical gelation approach, after performing an optical exposure at low temperature and making a particle condense.

[0025] As for a water dispersing element, it is desirable to **** the nonvolatile matter to 20% of the weight or more. If lower than 20 % of the weight, since the absolute number of the particle in a water dispersing element will decrease, while being hard coming to condense particles, the crack by drying shrinkage etc. tends to go into a coat, and it is hard to obtain a uniform gelation object. Although not limited, since especially the upper limit of a nonvolatile matter has the bad workability when becoming hyperviscosity and applying to a base material when it exceeds 70 % of the weight, it is not desirable.

[0026] in order that [which explained the gelation object obtained by this invention method until now] it may condense and gel and inorganic [in an emulsion] or an organic particle may coat-ize like, maintaining the particle condition mostly -- abbreviation -- the opening between spherical particles serves as a special gelation object which exists in a coat as puncturing. For this reason, the magnitude of puncturing of the gelation object obtained receives effect in inorganic [in a water dispersing element], or the magnitude of an organic particle. For example, as for the gelation object obtained, an activity of the thing 10 micrometers or less of the mean particle diameter of the particle in a water dispersing element (before condensing) formed much detailed and uniform puncturing with an average diameter of 500nm or less.

[0027] Moreover, if particle size distribution of the particle in a water dispersing element is made into Sharp, the distribution degree of the diameter of puncturing can be made into Sharp. Moreover, if the magnitude and solid content concentration of a particle in a water dispersing element are controlled, it is possible to control freely the magnitude and the consistency (the number of puncturing per unit volume) of puncturing. By furthermore choosing the raw material and property of a particle suitably according to an application, the porous membrane of this invention is applicable to various fields.

[0028] For example, it is useful also in the field of the special film related field which has an air

filter, a filtration membrane and semipermeable membrane, and selective permeability, a dc-battery separator or a recorded material, etc., etc.

[0029]

[Example] Although this invention is further explained in full detail according to an example below, the following example does not restrict this invention and all the things done for modification implementation in the range which does not deviate from before and the after-mentioned meaning are included by the technical range of this invention. In addition, that it is especially with "%" and the "section" in the following examples shall express "% of the weight" and the "weight section", unless it refuses.

[0030] the flask equipped with example 1 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser -- the ion-exchange-water 170 section and NONIPORU 200 (polyethylene-glycol nonylphenyl ether system emulsifier by Sanyo Chemical Industries, Ltd.) -- the 17 sections and new pole PE-64 (polyethylene-glycol-polypropylene-glycol block-copolymer system emulsifier by Sanyo Chemical Industries, Ltd.) -- 2 section preparation -- it heated at 45 degrees C, blowing nitrogen gently. The monomer mixture which consists of the methyl-methacrylate 292 section, the butyl acrylate 23 section, and the styrene 135 section was put into the dropping funnel, and 25% of them was dropped in the flask.

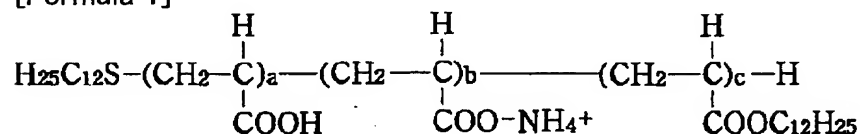
[0031] Then, the 15 sections and the 3% water-solution 15 section of ammonium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 62 of the remaining monomer mixture and a sodium hydrogensulfite section and the 1% water-solution 62 section of ammonium persulfate were dropped for 3 hours after 30 minutes, respectively. During dropping, the temperature in a flask was held at 50-54 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aquosity resin dispersant [1] which the polymer particle with 50.2% of nonvolatile matters, a pH [2.1], and a mean particle diameter of 120nm distributed was obtained.

[0032] this aquosity resin dispersant [1] 100 section -- beforehand -- the zinc-sulfate 100 section -- receiving -- the 25% aqueous ammonia 108 section, in addition produced 48% water solution of ammonium-sulfate zinc complexes -- 6 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [1] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #20 -- using -- spreading -- service water -- a dispersing element [1] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 60% of humidity -- it put into a constant humidity in a plane for 15 minutes, and gelation of the polymer particle in a moisture powder body whorl and desiccation of a coat were performed. Desiccation thickness obtained the gelation object [1] which is 25 micrometers.

[0033] It heated at 80 degrees C, having taught the ion-exchange-water 322 section to the flask equipped with example 2 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Churning mixing of the methyl-methacrylate 265 section, the divinylbenzene 117 section, the gamma-methacryloxypropyl-trimethoxy-silane 8 section, the 20% water-solution 70 section of the emulsifier represented with the following type, the ion-exchange-water 175 section, and the 25% aqueous ammonia 3 section was carried out, the pre emulsion for dropping was prepared, and 2% of them was dropped at the flask.

[0034]

[Formula 1]



[0035] (However, as an average of an emulsifier, the sum total of a and b is 20 and c is 1 or 2.) Moreover, each monomer unit shall be combined at random by the intramolecular of an emulsifier.

Then, the 5% water-solution 20 of potassium persulfate section was poured into the flask,

dropping of the remaining pre emulsions was started after 30 minutes, and dropping was ended 5 hours after. During dropping, the temperature in a flask was held at 78-82 degrees C, 20 section addition charge of the 2% water solution of potassium persulfate was carried out after dropping termination, it agitated at this temperature further for 1 hour, the polymerization was terminated, and the aqueous resin dispersant [2] which the polymer particle with 40.4% of nonvolatile matters, a pH [8.1], and a mean particle diameter of 176nm distributed was obtained.

[0036] 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 in this aqueous resin dispersant [2] 100 section -- the 7.5 sections and TPA-4380 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) -- 1 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [2] was obtained. # except for having used the bar coating machine of 26 -- an example 1 -- the same -- carrying out -- spreading -- service water -- in the dispersing element [2], coating and gelation, and when it dried, the gelation object [2] of 25 micrometers of desiccation thickness was obtained.

[0037] It heated at 70 degrees C, having taught the ion-exchange-water 183 section and the Aqualon HS-10 (reactant emulsifier of Dai-Ichi Kogyo Seiyaku nature) 1 section to the flask equipped with example 3 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Mixed churning of the seven sections and the ion-exchange-water 194 section was carried out for Aqualon HS-10 with the methyl-methacrylate 298 section, the 2-ethylhexyl acrylate 141 section, the styrene 50 section, the acrylic-acid 6 section, and the glycidyl methacrylate 5 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0038] Then, the 20 sections and the 3% water-solution 20 section of potassium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 37 of the remaining pre emulsions and a sodium hydrogensulfite section and the 3% water-solution 37 section of potassium persulfate were dropped for 3 hours after 15 minutes, respectively. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueous resin dispersant [3] which the polymer particle with 50.9% of nonvolatile matters, a pH [1.7], and a mean particle diameter of 118nm distributed was obtained.

[0039] 45% water solution of ammonium-carbonate zinc complexes which added the zinc-oxide 46 section, the ammonium-hydrogencarbonate 49 section, and the 25% aqueous ammonia 116 section beforehand, and was made in this aqueous resin dispersant [3] 100 section -- 10 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [3] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #20 -- using -- spreading -- service water -- a dispersing element [3] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- it put into a constant humidity in a plane for 1 minute, and, subsequently dried within the 80-degree C dryer for 1 minute, and gelation of the polymer particle in a moisture powder body whorl and desiccation of a coat were performed. Desiccation thickness obtained the gelation object [3] which is 25 micrometers.

[0040] It heated at 70 degrees C, having taught the ion-exchange-water 275 section to the flask equipped with example 4 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Mixed churning of the butyl acrylate 315 section, the divinylbenzene 135 section, and the high tenor N-08 (Dai-Ichi Kogyo Seiyaku polyethylene-glycol alkylphenyl ethereal sulfate ammonium) 16 section that are the 27 sections and an anion system emulsifier about NONIPORU 200 (emulsifier of the Sanyo Chemical Industries polyethylene-glycol nonylphenyl ether system) was carried out with the ion-exchange-water 214 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0041] Subsequently, the five sections were added for 5% water solution of 2 and 2'-azobis (2-amidinopropane) dihydrochloride in the flask. The remaining pre emulsions were dropped for 3 hours after 20 minutes. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueous resin dispersant [4] which the polymer particle with

49.8% of nonvolatile matters, a pH [1.8], and a mean particle diameter of 132nm distributed was obtained.

[0042] 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 in this aqueosity resin dispersant [4] 100 section -- 10 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [4] was produced and the gelation object [4] whose desiccation thickness is 25 micrometers was obtained like the example 1.

[0043] It heated at 80 degrees C, having taught the 20% water-solution 80 of the emulsifier used in the ion-exchange-water 223 section and the example 2 section, and the 25% aqueous ammonia 3 section to the flask equipped with example 5 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser, and blowing nitrogen into it gently. Churning mixing of the methyl-methacrylate 324 section, the divinylbenzene 36 section, the 20% water-solution 36 section of the emulsifier used in the example 2, and the 25% aqueous ammonia 2 section and the ion-exchange-water 142 section was carried out, the pre emulsion for dropping was prepared, and 15% of them was dropped at the flask.

[0044] Then, the 1% water-solution 10 of a sodium hydrogensulfite section and the 5% water-solution 24 section of potassium persulfate were added in the flask. Dropping of the remaining pre emulsions was begun after 30 minutes, and dropping was ended over 4 hours. During dropping, the temperature in a flask was held at 78-82 degrees C, and 20 section addition charge of the potassium persulfate water solution was carried out 2% 2 hours after dropping initiation.

Furthermore, after dropping termination, 20 sections of 2% of potassium persulfate water solutions were thrown in, and they were agitated for 3 hours.

[0045] Next, it was dropped in the flask, having pre applied [which agitated the 20% water-solution 4 of the emulsifier used in the ethyl-acrylate 30 section, the N-vinyl-pyrrolidone 8 section, the glycidyl methacrylate 2 section, and the example 2 section, and the ion-exchange-water 16 section, and was prepared] it for 30 minutes. During dropping, the temperature in a flask was held at 68-72 degrees C, the 20 sections of 2% water solutions of potassium persulfate were thrown in after dropping termination, it agitated at this temperature further for 1 hour, and the polymerization was terminated. The aqueosity resin dispersant [5] which the polymer particle with 42.3% of nonvolatile matters, a pH [8.0], and a mean particle diameter of 50nm distributed was obtained.

[0046] this aqueosity resin dispersant [5] 100 section -- TPA-4390 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) -- 3 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [5] was produced and the gelation object [5] of 25 micrometers of desiccation thickness was obtained like the example 2.

[0047] the flask equipped with example 6 dropping funnel, an agitator, nitrogen installation tubing, the thermometer, and the reflux condenser -- the ion-exchange-water 183 section and Aqualon HS-10 -- 1 section preparation -- it heated at 70 degrees C, blowing nitrogen gently. Mixed churning of the seven sections and the ion-exchange-water 194 section was carried out for Aqualon HS-10 with the methyl-methacrylate 155 section, the 2-ethylhexyl acrylate 284 section, the styrene 50 section, the acrylic-acid 6 section, and the glycidyl methacrylate 5 section, the pre emulsion for dropping was prepared, and 5% of them was dropped in the flask.

[0048] Then, the 20 sections and the 3% water-solution 20 section of potassium persulfate were added for 1% water solution of a sodium hydrogensulfite in the flask. The 1% water-solution 37 of the remaining pre emulsions and a sodium hydrogensulfite section and the 3% water-solution 37 section of potassium persulfate were dropped for 3 hours after 15 minutes, respectively. During dropping, the temperature in a flask was held at 68-72 degrees C, it agitated at this temperature after dropping termination further for 1 hour, and the polymerization was terminated. The aqueosity resin dispersant [6] which the polymer particle with 50.6% of nonvolatile matters, a pH [1.8], and a mean particle diameter of 128nm distributed was obtained.

[0049] 48% water solution of ammonium-sulfate zinc complexes which added the these aqueosity resin dispersant [6] 10 section and the aqueosity resin dispersant [2] 90 section obtained in the example 2, and produced TPA-4380 (Toshiba Silicone polyether denaturation silicone system sensible-heat gelling agent) like the one section and an example 1 -- 5 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [6] was obtained. the 100-

micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #24 -- using -- spreading -- service water -- a dispersing element [4] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- after putting into a constant humidity in a plane for 1 minute and making it gel, it was made to dry within 80-degree C hot air drying equipment for 1 minute, and the gelation object [6] whose desiccation thickness is 25 micrometers was produced.

[0050] To the aqueosity resin dispersant [1] 87 section obtained in the example 7 example 1, it is 2, 2, and 4-trimethyl. --The 1 and 3-pentanediol monochrome iso butyrate 13 section was added, and it agitated well. 48% water solution of ammonium-sulfate zinc complexes produced like the example 1 to this aqueosity resin dispersant -- 5 ***** -- good -- agitating -- spreading -- service water -- the dispersing element [7] was obtained. the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer -- the bar coating machine of #26 -- using -- spreading -- service water -- a dispersing element [7] -- coating -- carrying out -- immediately -- the constant temperature of 80 degrees C and 96% of humidity -- after putting into a constant humidity in a plane for 1 minute and making it gel, it was made to dry within 80-degree C hot air drying equipment for 1 minute, and the gelation object [7] whose desiccation thickness is 25 micrometers was produced.

[0051] the aqueosity resin dispersant [3] obtained in the example of comparison 1 example 3 -- as it is -- spreading -- service water -- it used as a dispersing element [8], applied to the 100-micrometer PET film with which 3-micrometer polyvinyl alcohol is applied as a primer layer by the bar coating machine of #30, and dried for 1 minute with 80-degree C hot air drying equipment. Desiccation thickness produced the sheet for a comparison [8] which is 25 micrometers.

[0052] The surface state of the sheet for a comparison [8] obtained in gelation object [1]- [7] obtained in each examples 1-7 and the example 1 of a comparison was expanded by 20,000 times using the scanning electron microscope (SEM), the formation condition of a hole was observed, and the result was summarized in a table 1. Moreover, the observation result of the product of examples 1 and 3 and the example 1 of a comparison was shown in drawing 2 -4. In the example 1, the gelation object of porosity like the pattern B in drawing 1 was obtained, and the gelation object of the porosity welded a little like Pattern C was obtained in the example 3 so that clearly from a table and drawing. However, it turns out that the thing of the example 1 of a comparison became a coat without a hole like Pattern A.

[0053]

[A table 1]

		表面状態	備 考
実 施 例	[1]	多 孔 質	計算T _g 90℃
	[2]	多 孔 質	高T _g モノマー架橋
	[3]	多 孔 質	計算T _g 30℃
	[4]	多 孔 質	低T _g モノマー架橋
	[5]	多 孔 質	コア・シェルタイプ
	[6]	多 孔 質	2種類ブレンド系
	[7]	多 孔 質	成膜助剤使用
比較用シート [8]		無孔	通常乾燥

[0054]

[Effect of the Invention] this invention method is an approach of obtaining the gelation object in

which much micropores by the gap of particles were made forming, by making inorganic [in a water dispersing element], or an organic particle condense maintaining the particle condition mostly, and coat-izing it. If inorganic [in a water dispersing element] or condensation of an organic particle is especially performed under the ambient atmosphere more than setting temperature and more than the same water vapor pressure as the saturated water vapor pressure in setting temperature, a much more uniform gelation object can be manufactured. Since much micropores are formed, in addition to this, the gelation object obtained by this invention method can be developed for the film related field or various applications.

[Translation done.]